The Solubility of Liquids in Liquids. The Partition of the Lower Acids between Water and Cottonseed Oil. Also the Partition of Formic Acid between Water and Various Organic Compounds

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A DISSERTATION

SUBMITTED TO THE BOARD OF UNIVERSITY STUDIES OF THE JOHNS HOPKINS UNIVERSITY IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

BY

NEIL E. GORDON

Baltimore, Maryland

June, 1917

EASTON, PA.:

ESCHENBACH PRINTING CO.

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THE SOLUBILITY OF LIQUIDS IN LIQUIDS. THE PARTITION OF THE LOWER ACIDS, PARTICULARLY FORMIC, BETWEEN WATER AND VARIOUS ORGANIC SOLVENTS[1]

That some substances dissolve when brought into contact with various liquids must have been one of the first observations that can be classed as chemical. In the last three decades the study of solutions has been the chief occupation of chemists. Yet our knowledge of solutions is still far from adequate and some of our conceptions are still not clear.

If we shake a portion of water with oxygen, another portion with ether, and a third with sugar, assuming constant temperature, equilibria are reached and we call the three solutions saturated, speaking of the concentrations of the three solutes in the water as their solubilities. The words "saturated and solubility" are used for all, but actually have quite different meanings in the three cases.

The solubility of the sugar is definite, since in that case the solid phase is pure sugar, unchanged in composition and concentration by its contact with the water. In the case of the oxygen and water, the only thing that we can determine is the ratio of the concentrations of oxygen in the two phases. Since the water vapor does not affect the partial pressure of the oxygen, this ratio is definite and independent of the water vapor present in the gas phase. As previously pointed out[2] while the solubility of the ether is definite, yet the solubility that we find is not the true solubility, i. e., the amount of ether taken up by water in contact with anhydrous ether. We can no more determine the solubility of ether in water than we can

[1] Contribution from the Chemical Laboratory of the Johns Hopkins University.

[2] Wroth and Reid: Jour. Am. Chem. Soc., **38**, 2316 (1916).

that of formic acid, since we cannot have a solution of either ether or formic acid in contact with the anhydrous liquid. We may hope that sometime a method, or formula, may be devised for finding the true, or ideal, solubility of ether in water, perhaps from the observed equilibrium of the solution of ether in water with one of water in ether, perhaps from some other data.

In the case of solid iodine, where the solubilities are true solubilities, Jakowkin[1] found the ratio of the solubilities in two solvents, S_a/S_b, remarkably near to the partition ratio, C_a/C_b, or r, measured with the same two solvents. He further found that r changes progressively, approaching more and more nearly the value S_a/S_b as the concentrations of iodine in the two solvents increase, i. e., as C_a/C_b approaches S_a/S_b as C_a and C_b aproach S_a and S_b.

As is well known, the partition ratio, r, remains constant with changing concentrations, only when the substance partitioned dissolves in both solvents in the same form. Furthermore, it is stipulated that the two solvents must be absolutely insoluble in each other, even when both contain large amounts of the common solute. This condition is, of course, never more than approximately fulfilled, the disturbing influences becoming greater, the higher the concentrations of the solute.

In the present investigation formic acid has been partitioned between water and the following solvents: cottonseed oil, kerosene, benzene, toluene, xylene, carbon tetrachloride, carbon disulphide and bromoform. The so-called solubilities of formic acid in these eight solvents and the solubilities of these liquids in formic acid have been determined.

If the solubility figure found for formic acid in benzene, say, were the ideal solubility and the partition ratio found were correct, then the product of these two should give the ideal solubility of formic acid in water which we cannot find directly. The ideal solubility from the data obtained from these eight solvents should be the same, or, since the several

[1] Zeit. phys. Chem., **18,** 590 (1895).

partition ratios vary with the concentrations, the values found should tend to approach some one limit, as the concentrations of formic acid in the non-aqueous solvents approach the solubilities of formic acid in these solvents.

In the case of carbon disulphide and water, and in that only, the partition ratio remained practically constant with changing concentration, being 1606 when the acid in the water layer was 8.4% and 1616 when this had increased to 54.8%. When carbon disulphide and formic acid are shaken together there is 1.28 g of the acid to 100 g carbon disulphide in the one layer and 4.66 g carbon disulphide to 100 g formic acid in the other. Even in this case 1.28 is not the ideal solubility of formic acid since the solution was in contact with a mixture of 95.55% formic acid and 4.45% carbon disulphide and not with the pure acid, but as in this case the mutual "solubilities" are the lowest and the partition ratio is the most nearly constant, this appears to be, by far, the most favorable case. Multiplying 1.28, the "solubility" of formic acid in carbon disulphide, by the partition ratio, 1616, we have 2068 as the ideal solubility of formic acid in water, i. e., 2068 g of the acid should be taken up by 100 g of water in contact with *anhydrous* formic acid, a condition which can, of course, never be realized. With the other seven solvents the products of the several solubilities by the respective partition ratios should approach 2068 as the concentrations increase. That is the figures in the last columns of Tables 1 and 7–12 should approach 2068 as we read down. The results are represented graphically in Fig. 1 in which these hypothetical ideal solubilities are plotted against the percentage of saturation of the non-aqueous layer. The curves as drawn extend only to 8%, not far enough to include all the points on the kerosene, cottonseed oil and bromoform curves. For very dilute solutions the figures obtained are more or less erratic on account of the difficulties involved in determining the small amounts of acid present in even large amounts of the oil layers, e. g., in the most dilute solution with carbon tetrachloride the amount of formic acid per 100 g of oil was only 0.0038 g.

Most of the series were terminated at 55% to 60% of formic acid in the water layer as it was thought that results with greater concentrations could not be trusted on account of mutual solubilities of the two solvents in presence of so much of the solute. But with cottonseed oil the concentration was carried up to 87.2% of formic acid in the water layer when there was 5.026 g of acid per 100 g of the oil layer while the solubility of the anhydrous acid in the oil is 8.68 g per 100 g. This gives us a point in the cottonseed oil curve at 58% for which the ordinate is 1179 which is well on the way to the figure indicated by the carbon disulphide curve.

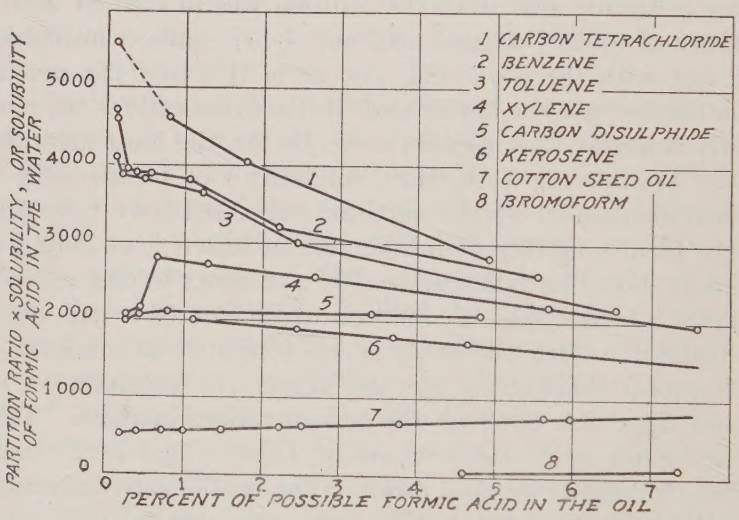

Fig. 1

It is interesting to note that cottonseed oil takes up only 58% as much formic acid from an 87% acid as from the 100% acid. On a molecular basis 73% of the molecules are formic acid, so it appears that the water in the acid is more than a diluent: it restrains the formic acid molecules from passing into the oil layer. A similar inference may be drawn from other experiments. In most cases where the water layer con-

tains over 50% of formic acid the oil layer takes up only 5% to 7% as much acid as from 100% formic acid.

The results with kerosene are regarded as unreliable as the oil layer was much colored at the higher concentrations indicating some sort of reaction.

Looking at the figure, there appears to be a tendency for the various curves to converge on the carbon disulphide line indicating an ideal solubility around 2000, though the bromoform curve is very low down and the one for cottonseed oil has a considerable distance to go. The xylene curve appears to cross the 2000 line. It is certainly hazardous to extrapolate from 6 or 8% to 100%.

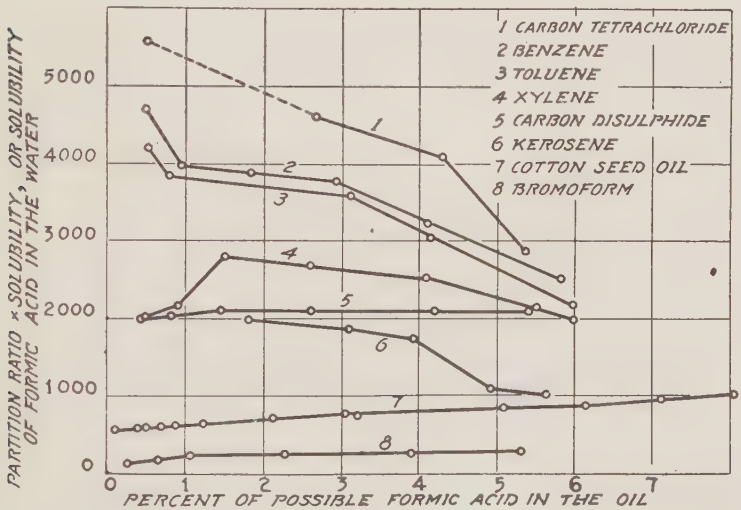

Fig. 2

In Fig. 2 the same data are presented on a different basis; the ordinates are the same but the abscissae are the percentage of formic acid in water layer at equilibrium. On this basis the curves are steeper and do not show as much tendency to converge though we have the advantage of having to extrapolate over a much shorter distance, as all of the curves go as far as 55% and one even to 87%.

The results obtained do not settle the question but it is hoped they do open it. One method of approach has been tried: better ones may be found. Even by this method more measurements are desirable at higher concentrations, with other solvents, and with other solutes. The results so far obtained have value as partition and solubility measurements. The degrees of association of formic acid in the various solvents can be calculated from the variation of the partition ratios.

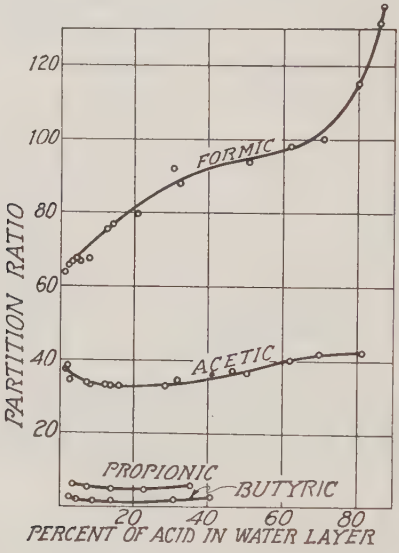

Fig. 3

As formic acid is a strong acid, its dissociation in the water layer influences the partition ratios, but as its lowest concentration was 0.24 N, at which it is only moderately dissociated and, as it turned out, the high concentrations are the ones which are of most interest from the present point of view, the dissociation may be disregarded. It is interesting to note that formic acid shows a real partition ratio in all cases even in dilute solution, which is in marked contrast to the behavior of silver perchlorate as found by Hill.[1]

[1] Jour. Am. Chem. Soc., **43**, 254 (1921).

Georgievics[1] partitioned formic acid between benzene and water. Calculating his results according to our method we obtain the following partition ratios:

% Acid	4.4	5.8	6.7	7.8	8.6	8.7	13.3	13.3	18.9	23.9
Ratio	370	261	400	302	264	562	304	347	269	298

Disregarding the sixth, the average of these is 316 which is not far from 292 the average of our results over the same range.

In addition to the experiments with formic acid, acetic, propionic and butyric were partitioned between cottonseed oil and water and acetic acid between kerosene and water. The partition ratios are plotted in Fig. 3. The proportion of the organic acid taken by the water layer increases rapidly as we go from formic to butyric. The formic acid curve bends sharply upward at about 70% of acid in the water layer. Acetic acid has a definite solubility in the oil but propionic and butyric have not. Formic is the only one of these that shows limited solubility in the other solvents.

Materials

Cottonseed Oil: The Wesson oil used was found to have an acid reaction. In order to eliminate this the oil was shaken with a dilute solution of barium hydroxide for an hour. It was then centrifuged and filtered, when it gave a perfectly neutral reaction.

Formic Acid: This was distilled under reduced pressure over anhydrous copper sulphate as suggested by Garner, Saxton and Parker. The pressure used was 120 mm, when the acid distilled over at 50°. This method was found to be a very satisfactory one. Beginning with an acid 89.2 percent pure, the first distillation resulted in an acid 96.5 percent, the second 98.2 percent, and the third distillation gave an acid 99.99 percent pure. This acid melted at 8.35° and had density 1.2170^{25}_{25}.[2] This anhydrous acid was used for the solubility work only. For the partition work, commercial acid was used

[1] Zeit. phys. Chem., **84,** 359 (1913).

[2] Am. Chem. Jour., **46,** 236 (1911); J., **1886,** 216.

since it was found to contain only water. The water it contained was calculated and added to the weight of water taken.

Acetic Acid: Like formic acid the commercial acid was used for the partition work. For the solubility the acid was purified by freezing. It was found that the number of freezings necessary to render it anhydrous could be cut down by introducing a crystal of the acid to prevent too great undercooling. It melted at 16.7°, and titrated 99.9 percent pure. Its density was 1.0445^{25}_{25}.

Propionic and Butyric Acids: These acids mixed in all proportions with both oil and water and thus it was not necessary to make them anhydrous. As their densities and titrations showed they contained only water as an impurity, they were used without further purification.

Organic Solvents: First class commercial grades of benzene, toluene, xylene, carbon tetrachloride, carbon disulphide, and bromoform were used. To insure purity, the boiling points and densities were taken and found to agree well with those given in the literature.

Waddell[1] found in his investigation that the same partition coefficient was given with purified benzene as with commercial benzene.

Standard Solutions: Standard solutions of approximately N/10 were prepared, and frequently standardized. The solutions were kept in large stock bottles from which they were siphoned into the burettes. The barium hydroxide bottle and burettes were protected from the air by tubes containing soda lime.

Water: Freshly distilled water was used.

Kerosene Oil: Commercial kerosene oil was distilled and the portion obtained between 180° and 260° was used in the partition work. It had a density of 0.798^{25}_{25}.

[1] Jour. Phys. Chem., **2**, 233 (1895).

Procedure

The filling, shaking and centrifuging of the bottles containing cottonseed oil, water and the respective acids was carried out approximately as the former work where the alcohols were used instead of the acids. It seemed necessary to shake the acids longer than the alcohols to obtain concordant results. The centrifuge was used only with the cottonseed oil and water.

Estimation of Acids in Non-aqueous Solvent Layers.—The oil layer containing the acid was drawn off by means of a special pipet, shaped similar to the Ostwald pycnometer. An amount of oil was taken out with the pipet sufficient to require about 10 cc of the barium hydroxide for neutralization. The oil was put into a 180-cc beaker containing about 80 cc of distilled water for titration. The oil, with ordinary stirring failed to give up its acid promptly, making the titration slow and uncertain. A mechanical stirrer was used and this accelerated the speed with which the acid passed from the oil into the water. Even under these conditions the end-point was not as accurate as it was in the water. In spite of all efforts the acid seemed to have a slight tendency to cling to the oil. The other organic solvents were handled similarly.

Estimation of Acid in Water Layer.—A small thin-walled glass bulb was weighed, partly filled from the water layer, sealed and reweighed. The bulb was then broken under water to avoid evaporation, and the amount of acid, which it contained was determined by titration.

The absolute solubilities of formic and acetic acids in cottonseed oil were found by shaking the oil and anhydrous acids in the constant temperature bath for four hours, and then estimating the amount of acid in the oil layer and the amount of oil in the acid layer by the titration method as just described. The absolute solubility of formic acid in the other organic solvents used and the solubility of the solvents in the formic acid were carried out in a similar manner.

Solubilities at 25°

Formic Acid in Cottonseed Oil			Cottonseed Oil in Formic Acid		
Sample	Found	In 100 g	Sample	Found	In 100 g
0.3154	0.0251	8.65	0.1656	0.0013	0.78
0.1656	0.0416	8.72	0.1141	0.0009	0.79
0.4437	0.0360	8.84	0.1086	0.0008	0.74
0.5019	0.0393	8.50	0.1142	0.0009	0.79
		Av. 8.68			Av. 0.77

Acetic Acid in Cottonseed Oil			Cottonseed Oil in Acetic Acid		
0.1421	0.0508	55.4	0.1016	0.0058	5.8
0.0858	0.0309	56.3	0.0996	0.0055	5.5
0.0831	0.0299	56.3	0.0616	0.0036	5.7
0.0684	0.0245	55.96	0.1373	0.0073	5.6
0.1008	0.0345	54.3	0.0894	0.0050	5.6
		Av. 55.7			Av. 5.6

Formic Acid in Benzene			Benzene in Formic Acid		
Sample	Found	In 100 g	Sample	Found	In 100 g
0.2718	0.0341	14.3	0.1825	0.0238	15.0
0.3300	0.0416	14.4	0.0992	0.01312	15.2
0.3950	0.0502	14.5	0.1455	0.0189	14.9
0.4277	0.0537	14.3	0.0030	0.0122	15.4
0.4197	0.0527	14.40			
		Av. 14.40			Av. 15.14

Formic Acid in Toluene			Toluene in Formic Acid		
0.2815	0.0284	11.20	0.1793	0.0149	9.08
0.3795	0.0376	10.98	0.1323	0.0110	9.06
0.2986	0.0295	10.96	0.0851	0.0071	9.10
0.3565	0.0358	11.17			
		Av. 11.08			Av. 9.08

Formic Acid in Xylene			Xylene in Formic Acid		
0.5440	0.0442	8.83	0.1009	0.0063	6.81
0.3535	0.0251	8.70	0.0790	0.0057	7.77
0.4480	0.0357	8.70			
		Av. 8.74			Av. 7.29

Solubilities at 25°

Formic Acid in Carbon Tetrachloride			Carbon Tetrachloride in Formic Acid		
0.1910	0.0069	(3.76)	0.0484	0.0030	6.60
0.3434	0.0115	3.45	0.0934	0.0062	6.95
0.3623	0.0119	3.40	0.0918	0.0063	7.31
0.3158	0.0105	3.44			
		Av. 3.43			Av. 6.95

Formic Acid in Carbon Disulphide			Carbon Disulphide in Formic Acid		
2.4628	0.0313	1.29	0.0631	0.0604	4.47
1.9878	0.0240	1.28	0.1429	0.1398	4.85
2.6070	0.0311	(1.21)			
4.7033	0.0549	(1.18)			
4.9431	0.0569	(1.16)			
7.461	0.0959	1.29			
		Av. 1.28			Av. 4.66

Formic Acid in Bromoform			Bromoform in Formic Acid		
1.9684	0.0475	2.47	0.1301	0.0362	25.2
1.2830	0.0310	2.47	0.1085	0.0220	25.4
3.2351	0.0767	2.42			
		Av. 2.45			Av. 25.3

Formic Acid in Kerosene			Kerosene in Formic Acid		
Sample	Found	In 100 g	Sample	Found	In 100 g
3.3003	0.0294	0.899	0.1003	0.0015	1.52
2.9977	0.0267	0.905	0.0681	0.0011	1.60
		Av. 0.897			Av. 1.56

Acetic Acid in Kerosene			Kerosene in Acetic Acid		
1.0690	0.1909	21.74	0.0735	0.0082	12.6
0.7638	0.1367	21.80	0.0802	0.0088	12.3
		Av. 21.77			Av. 12.4

Partition Experiments

The results are given in the tables below, no completed determination being omitted, the first column showing the final percentage of acid in the water layer, the next three the amounts of water, oil and acid weighed in, while the fifth and sixth give the amounts of acid found in the two layers, the sum of these should equal the weight of acid in column four. In the seventh is found the molecular partition ratio or the acid dissolved by 1 mol. of water divided by that dissolved by 1 mol. of the oil. The m. wt. of cottonseed oil was assumed to be 885. In the case of kerosene this ratio is omitted. The next column gives the partition ratio for equal weights of water and oil and the last gives this weight ratio multiplied by the solubility of the acid in the oil when this is known.

TABLE 1

Partition of Formic Acid between Cottonseed Oil and Water

% Acid	Water	Oil	Acid	Weight acid in		Partition ratios		Weight ratio × 8.68
				Water	Oil	Molecular	Weight	
1.1	15.42	66.85	0.183	0.169	0.0115	1.29	63.6	552
2.3	16.94	70.53	0.423	0.399	0.0253	1.33	65.7	570
3.7	14.57	75.37	0.595	0.556	0.0430	1.36	66.8	580
4.2	22.54	72.63	1.036	0.990	0.0471	1.38	67.8	588
5.5	22.66	67.69	1.385	1.326	0.0592	1.36	66.9	581
8.1	12.05	81.52	1.163	1.064	0.1064	1.38	67.7	588
12.7	27.00	63.19	4.077	3.945	0.1224	1.54	75.4	654
14.4	6.84	5.91	1.166	1.152	0.0130	1.56	76.5	664
20.9	13.11	20.47	3.556	3.470	0.0680	1.62	79.7	692
30.3	5.57	6.576	2.500	2.429	0.0323	1.87	91.9	798
32.4	12.62	22.87	6.168	6.045	0.1192	1.81	88.8	771
51.1	4.54	5.051	4.827	4.747	0.0563	1.91	93.9	815
62.5	3.65	5.857	6.258	6.087	0.0997	1.99	97.9	850
71.3	3.16	4.981	8.043	7.854	0.1241	2.03	99.5	864
80.7	1.79	6.102	7.720	7.463	0.2222	2.34	114.8	996
86.3	0.799	7.728	5.493	5.023	0.3705	2.67	131.1	1138
87.2	0.728	8.589	5.894	4.972	0.4317	2.76	135.8	1179

TABLE 2

Partition of Acetic Acid between Cottonseed Oil and Water

% Acid	Water	Oil	Acid	Weight acid in		Partition ratios		Weight ratio × 55.7
				Water	Oil	Molecular	Weight	
1.9	25.84	68.32	0.544	0.5105	0.0363	0.757	37.2	2071
2.1	24.32	66.23	0.550	0.5130	0.0364	0.781	38.4	2137
2.4	26.70	65.86	0.696	0.6504	0.0463	0.705	34.6	1930
7.5	27.51	71.33	2.408	2.238	0.1711	0.690	33.9	1888
8.2	26.31	64.31	2.513	2.346	0.1718	0.671	33.4	1859
12.7	26.68	68.80	4.185	3.877	0.3006	0.677	33.3	1853
14.1	28.28	69.97	4.9751	4.636	0.3471	0.672	33.0	1840
16.2	24.75	67.27	5.195	4.791	0.3940	0.673	33.1	1841
28.9	13.13	25.64	5.673	5.345	0.3177	0.667	32.9	1830
31.8	11.13	25.35	5.534	5.178	0.3453	0.695	34.2	1903
46.9	4.38	5.950	4.044	3.875	0.1424	0.752	36.9	2059
50.9	4.360	6.064	4.729	4.516	0.1720	0.743	36.5	2035
62.1	1.387	7.574	2.586	2.270	0.3118	0.809	39.7	2212
70.2	1.001	7.572	2.794	2.361	0.4311	0.843	41.4	2308
81.8	1.958	5.975	9.574	8.827	0.6483	0.845	41.5	2314

TABLE 3

Partition of Propionic Acid between Cottonseed Oil and Water

% Acid	Water	Oil	Acid	Weight acid in		Partition ratios	
				Water	Oil	Molecular	Weight
3.4	38.15	48.33	1.620	1.347	0.2819	0.123	6.05
7.4	39.75	42.39	3.836	3.165	0.6580	0.104	5.13
14.3	20.05	20.09	4.045	3.335	0.7240	0.094	4.62
23.0	15.09	20.88	5.855	4.502	1.358	0.093	4.59
36.2	3.416	7.705	2.744	1.938	0.7779	0.114	5.60
59.8	2.988	5.516	5.311	4.438	0.8959	0.186	9.14
62.5	0.8750	7.750	2.853	1.458	1.366	0.192	9.45
67.3	0.4755	8.919	2.873	0.979	1.874	0.199	9.79

TABLE 4

Partition of Butyric Acid between Cottonseed Oil and Water

% Acid	Water	Oil	Acid	Weight acid in		Partition ratios	
				Water	Oil	Molecular	Weight
2.7	16.135	24.590	0.747	0.4526	0.2764	0.0508	2.495
5.0	16.568	25.095	1.612	0.8798	0.7350	0.0369	1.813
9.2	6.530	6.562	1.164	0.6615	0.4906	0.0276	1.355
14.0	3.139	6.755	1.308	0.5106	0.7880	0.0284	1.395
30.5	3.911	6.597	3.458	1.714	1.692	0.0348	1.709
41.3	1.802	6.590	3.203	1.268	1.948	0.0484	2.380

TABLE 5

Partition of Formic Acid between Kerosene and Water

% Acid	Water	Oil	Acid	Weight acid in		Partition ratio Weight ratio	Weight ratio × 0.897
				Water	Oil		
17.9	10.634	65.717	2.324	2.316	0.00648	2209	1981
30.9	9.801	72.723	4.452	4.388	0.01586	2052	1841
38.9	9.778	65.189	6.283	6.224	0.02146	1933	1734
43.2	2.547	7.422	1.945	1.936	0.00308	1831	1642
59.8	2.725	5.645	4.160	4.060	0.00714	1180	1058
66.3	3.153	30.950	6.400	6.200	0.05358	1136	1019

TABLE 6

Partition of Acetic Acid between Kerosene and Water

% Acid	Water	Oil	Acid	Weight acid in		Partition ratio Weight ratio	Weight ratio × 21.77
				Water	Oil		
9.1	7.110	32.024	0.730	0.7127	0.02164	1483	32300
17.0	6.027	30.676	1.392	1.236	0.05796	1086	23600
27.2	6.786	29.831	2.665	2.532	0.1332	836	18200
46.9	2.503	8.479	2.330	2.214	0.09804	765	16700
59.2	2.819	6.243	4.273	4.089	0.1217	744	16200

TABLE 7

Partition of Formic Acid between Benzene and Water

% Acid	Water	Oil	Acid	Weight acid in		Partition ratios		Weight ratio × 14.40
				Water	Oil	Molecular	Weight	
5.3	20.61	74.21	1.138	1.146	0.0126	75.1	327	4710
6.4	11.46	89.07	0.742	0.716	0.0175	73.5	319	4590
9.9	19.96	82.54	2.195	2.192	0.0329	63.5	275	3960
13.6	21.71	65.42	3.444	3.432	0.0382	62.4	270	3890
18.5	28.39	51.66	6.506	6.437	0.0434	62.3	270	3890
29.2	10.30	28.71	4.395	4.258	0.0449	61.0	264	3810
41.2	12.71	32.92	9.126	8.894	0.1060	50.8	220	3170
58.2	3.272	40.73	5.096	4.695	0.3279	41.1	178	2570

TABLE 8

Partition of Formic Acid between Toluene and Water

% Acid	Water	Oil	Acid	Weight acid in		Partition ratios		Weight ratio × 11.08
				Water	Oil	Molecular	Weight	
5.3	21.04	79.04	1.174	1.177	0.0118	74.0	378	4190
7.9	20.43	64.20	1.799	1.761	0.0158	68.5	350	3880
16.5	10.319	88.00	2.086	2.039	0.0498	68.5	349	3870
31.0	9.210	84.70	4.257	4.148	0.1166	64.0	327	3620
41.7	5.618	30.87	4.181	4.019	0.0837	52.8	270	2990
59.7	3.276	32.68	5.186	4.834	0.2391	39.5	202	2230

TABLE 9

Partition of Formic Acid between Xylene and Water

% Acid	Water	Oil	Acid	Weight acid in		Partition ratios		Weight ratio × 8.74
				Water	Oil	Molecular	Weight	
5.0	10.42	83.55	0.561	0.5521	0.0190	39.7	233	2040
5.1	9.867	94.58	0.559	0.5355	0.0225	38.6	228	1990
8.6	11.24	86.25	1.185	1.158	0.0362	41.6	245	2140
9.6	9.891	76.12	1.066	1.047	0.0319	42.8	252	2210
15.0	10.41	71.74	1.889	1.835	0.0411	52.4	308	2690
15.6	10.85	79.05	2.036	2.006	0.0439	56.5	334	2920
25.6	10.03	67.34	3.576	3.460	0.0778	50.8	299	2610
26.4	10.29	69.27	3.795	3.697	0.0776	54.5	321	2800
40.4	6.136	30.50	4.308	4.171	0.0680	51.8	305	2660
41.2	5.881	38.13	4.248	4.125	0.0963	47.2	278	2430
55.2	3.870	29.86	5.036	4.760	0.1498	41.9	245	2160
55.7	3.994	38.84	5.382	5.026	0.1923	43.1	254	2220
60.3	2.660	84.32	4.830	4.036	0.5611	38.7	228	1990

TABLE 10

Partition of Formic Acid between Carbon Tetrachloride and Water

% Acid	Water	Oil	Acid	Weight acid in		Partition ratios		Weight ratio × 3.43
				Water	Oil	Molecular	Weight	
5.8	10.291	120.3	0.6534	0.635	0.00456	1910	1630	5590
8.6	9.978	107.4	0.9572	0.942	0.00861	1380	1180	4040
17.5	9.908	135.6	2.135	2.102	0.01541	2190	1870	6410
26.9	10.175	125.0	3.792	3.747	0.03416	1580	1350	4620
43.2	6.160	67.76	4.617	4.506	0.04213	1380	1180	4030
58.9	3.299	61.08	4.873	4.735	0.1040	990	840	2890

TABLE 11

Partition of Formic Acid between Carbon Disulphide and Water

% Acid	Water	Oil	Acid	Weight acid in		Partition ratios		Weight ratio × 1.28
				Water	Oil	Molecular	Weight	
4.8	10.24	122.6	0.514	0.512	0.00390	3720	1570	1991
8.4	10.48	115.3	0.981	0.965	0.00661	3800	1606	2056
14.6	11.36	122.0	1.962	1.942	0.01281	3850	1628	2084
25.7	10.21	112.0	3.583	3.536	0.02403	3820	1614	2066
41.6	5.406	125.3	3.966	3.850	0.05497	3840	1623	2077
54.8	6.244	121.7	7.763	7.565	0.09122	3830	1616	2068

TABLE 12

Partition of Formic Acid between Water and Bromoform

% Acid	Water	Oil	Acid	Weight acid in		Partition ratios		Weight ratio × 2.45
				Water	Oil	Molecular	Weight	
3.1	9.746	243.0	0.5734	0.3084	0.2771	1.98	27.8	68
6.9	10.28	189.1	1.123	0.7613	0.3407	2.93	41.1	101
10.8	11.03	177.1	1.660	1.336	0.3121	4.87	68.7	168
23.1	10.39	192.3	3.898	3.123	0.7580	5.43	76.3	187
39.0	5.286	53.51	3.792	3.378	0.3630	6.70	94.2	231
53.6	3.430	58.99	4.762	3.960	0.7142	6.79	96.3	236

Summary

Formic acid has been partitioned at 25° between water and cottonseed oil, kerosene, benzene, toluene, xylene, carbon tetrachloride, carbon disulphide and bromoform. Acetic acid has been partitioned between water and cottonseed oil and kerosene, and propionic and butyric acids between cottonseed oil and water. The solubilities of these acids have been determined in the solvents named and vice versa so far as these were limited.

An attempt has been made to get clearer ideas of the relations involved when liquids are miscible in all proportions.

BIOGRAPHY

Neil Elbridge Gordon was born October 7, 1885 in Spafford, New York. He received his grammer school education in district schools at Spafford.

He entered Homer High School in the fall of 1902 and was graduated in 1904. In the fall of 1908 he entered Syracuse University, New York, from which he was graduated with a degree of Ph.B. in 1911. In the spring of 1912 he received the degree of M.A. from the same institution. He continued his graduate work at Syracuse University until the fall of 1913, at which date he took a teaching position at The Park School, Baltimore, Md. He was engaged in this institution until the fall of 1916, when he entered Johns Hopkins University. He was graduated from Johns Hopkins Uhniversity with the degree of Ph.D. in June 1917.